



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/NL93/00026  <b>(22) International Filing Date:</b> 26 January 1993 (26.01.93)  <b>(30) Priority data:</b> 9200150                      28 January 1992 (28.01.92)      NL 9200530                      23 March 1992 (23.03.92)        NL  <b>(71) Applicant (for all designated States except US):</b> DSM N.V. [NL/NL]; Het Overloon 1, NL-6411 TE Heerlen (NL).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only) :</b> NOOYEN, Godefridus, Arnoldus, Henricus [NL/NL]; Oranjestraat 9, NL-5981 CA Helden (NL). OOSTRA, Hendrikus [NL/NL]; Mol- enstraat 53, NL-6116 CC Susteren (NL).		<b>(74) Agent:</b> KLEIBORN, Paul, Erik; Octrooibureau DSM, P.O. Box 9, NL-6160 MA Geleen (NL).  <b>(81) Designated States:</b> CA, FI, JP, KR, NO, RU, UA, US, Eu- ropean patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the</i> <i>claims and to be republished in the event of the receipt of</i> <i>amendments.</i>
<b>(54) Title:</b> ETHYLENE POLYMER HAVING AN INTRINSIC VISCOSITY OF AT LEAST 4 dl/g AND A METHOD FOR THE PREPARATION THEREOF  <b>(57) Abstract</b>  <p>The invention relates to an ethylene polymer having an intrinsic viscosity of at least 4 dl/g, which has a maximum draw ratio of at least 20, is pulverulent, has a bulk density of at most 300 kg/m<sup>3</sup> and has an amount of catalyst residues of less than 50 ppm. The invention also relates to a method for the preparation of a pulverulent ethylene polymer having an intrinsic viscosity of at least 4 dl/g through polymerization of ethylene or of a mixture of ethylene and not more than 2 mol % higher olefins at a temperature below 80 °C and an ethylene pressure below 0.2 MPa in the presence of a catalyst having a specific surface area of at most 150 m<sup>2</sup>/g. It further relates to articles composed of the ethylene polymer.</p>		

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ETHYLENE POLYMER HAVING AN INTRINSIC VISCOSITY  
OF AT LEAST 4 dl/g AND  
A METHOD FOR THE PREPARATION THEREOF

The invention relates to an ethylene polymer having an intrinsic viscosity of at least 4 dl/g and a method for the preparation thereof. An ethylene polymer of this type is disclosed in WO 87/03288. The ethylene polymer described in this publication can be stretched at temperatures below its melting point. To this end, the polymer is compressed to form a film, which can be stretched to at least 15 times its size at temperatures of 60-145°C. The stretched articles have a tensile strength of greater than 15 g/den (1.3 GPa) and a modulus of elasticity of greater than 500 g/den (45 GPa). The ethylene polymer is prepared through polymerisation of ethylene in the presence of a vanadium-containing catalyst at temperatures of, for example, -40°C to 20°C and pressures of less than 0.2 MPa absolute pressure. The polymerisation is carried out in the presence of a homogeneous vanadium catalyst or a vanadium catalyst applied to a support.

If the ethylene polymers according to WO 87/03288 are prepared using a homogeneous vanadium catalyst, the shape of the polymer obtained is irregular. The polymer has the macroscopic form of fragments and threads having dimensions of the order of one centimetre. Ethylene polymer in such a form is not or barely processable on an industrial scale.

If the ethylene polymers according to WO 87/03288 are prepared using a heterogeneous vanadium catalyst, such as a vanadium catalyst on a silica support (see the examples in WO 87/03288), the amount of catalyst residues in the polymer is high. In the examples this is 56-2310 ppm of

2.

vanadium. Such high contents of catalyst residues are undesirable. The amount of catalyst residues is calculated  
5 in a known manner from the polymer yield and the amount of active catalyst component (vanadium or titanium) which is supplied to the reactor.

According to WO 87/03288, comparative experiment F, titanium-containing catalysts having a high catalytic  
10 activity give a polymer which is not readily stretchable. The maximum degree of stretching is 5 at a stretching temperature of 100°C.

According to the invention there is provided an ethylene polymer which has a maximum draw ratio of at least  
15 20, is pulverulent, has a bulk density of at most 300 kg/m<sup>3</sup> and has an amount of catalyst residues of less than 50 ppm.

It has been found that some catalysts, under specific conditions during polymerisation, lead to a highly stretchable ethylene polymer, specifically when the  
20 polymerisation of ethylene or of a mixture of ethylene and not more than 5 mol% higher olefins is carried out at a temperature of at most 80°C and an ethylene pressure of at most 0.2 MPa in the presence of a transition metal catalyst having a specific surface area of at most 150 m<sup>2</sup>/g.  
25 Preferably, the specific surface area is at most 50 m<sup>2</sup>/g and more particularly at most 10 m<sup>2</sup>/g. The specific surface area is determined with the aid of ASTM standard D 3663-78. Pressures are indicated as absolute pressure in Pa.

The catalysts which are used according to the  
30 invention are transition metal catalysts known under the name Ziegler catalysts. Catalysts of this type can be prepared in a known manner. The following may be mentioned as transition metals which can occur in the Ziegler catalysts: vanadium, titanium, zirconium, hafnium and  
35 chromium. Preferably, the catalyst according to the invention is a titanium-containing catalyst having a high catalytic activity. Preferably, the catalysts which are used according to the invention have a yield of more than 800 g of polyethylene/g of catalyst under polymerisation

conditions such that the ethylene pressure is 0.07 MPa and the polymerisation temperature 60°C. Preferably, the catalysts are applied to a support which contains magnesium, more specifically magnesiumchloride. Preferably, the Mg/Ti molar ratio in such a catalyst is at least 5 and in particular at least 10. The following may be mentioned as examples of very suitable catalysts: UM-1<sup>R</sup> from Toho Titanium and Lynx 715<sup>R</sup> from Catalyst Resources Inc.

The catalysts according to the invention can be used in a known manner. According to the invention, polymerisation can be carried out in a slurry process or in a gas phase process. Inert solvents such as hexane, heptane and kerosene can be used as dispersing agents. Known co-catalysts, such as organoaluminium compounds or dialkyl compounds of, for example, Mg, Zn or Cd can be used. In this context see, for example, EP-A-114526, page 16, line 20 to page 18, line 22.

According to the invention, the temperature during polymerisation is at most 80°C. If the polymerisation temperature is too high, a polymer is obtained which is not readily stretchable. Preferably, the polymerisation temperature is at most 70°C.

The ethylene pressure during polymerisation is at most 0.2 MPa, preferably at most 0.15 MPa and in particular at most 0.1 MPa. If the ethylene pressure is too high, a polymer is obtained which is not readily stretchable.

It has been found that a stretchable ethylene polymer which can be obtained according to the invention is pulverulent, has a bulk density of at most 300 kg/m<sup>3</sup> and contains an amount of catalyst residues of less than 50 ppm. If the bulk density is higher than 300 kg/m<sup>3</sup>, the maximum degree of stretching is adversely affected. Preferably, the ethylene polymer has a bulk density of at most 250 kg/m<sup>3</sup>. More particularly, the ethylene polymer according to the invention has a bulk density of at most 200 kg/m<sup>3</sup>. The bulk density of polymer powder is determined in accordance with DIN 53466/A, and the particle size of pulverulent catalyst

is determined with the aid of laser light diffraction in a Malvern<sup>R</sup> particle size analyser.

5           The ethylene polymer according to the invention can further be characterized in that it has a lamella thickening factor of more than 1.5, measured after a thermal treatment of 75 hours at 125°C. The the lamella thickness can be  
10           determined using transmission electronmicroscopy. For the determination of the lamella thickening factor  $Q$  as defined according to the invention, the lamella thickness is measured of a sample of the ethylene polymer as polymerized ( $L_b$ ) and is also measured after a thermal treatment of the sample of 75 hours at 125°C ( $L_a$ ). The lamella thickening  
15           factor  $Q$  is defined as  $(L_a - L_b)/L_b$ . It was found that a small lamella thickening factor leads to a material which is not readily stretchable. Preferably the ethylene polymer has a lamella thickening factor of at least 2.0.

          The ethylene polymer obtained according to the  
20           invention is pulverulent instead of in the form of fragments or threads, such as are obtained using the homogeneous vanadium catalysts according to WO 87/03288. The polymerisation takes place with a relatively high catalyst activity. The amount of catalyst residues is low,  
25           specifically less than 50 ppm. The amount of catalyst residues is calculated from the polymer yield and the amount of active catalyst component metered in is expressed in ppm with respect to the total amount of polymer. In particular, the amount of catalyst residues is less than 25 ppm.

30           The intrinsic viscosity of the ethylene polymer according to the invention, determined in decalin at 135°C in accordance with ASTM standard D 4020, is at least 4 dl/g. The relative viscosity is in particular 8-40 dl/g. The ethylene polymer is a linear polyethylene having fewer than  
35           10 side chains per 1,000 carbon atoms and preferably having fewer than 3 side chains per 1,000 carbon atoms, or a polyethylene of this type which also contains minor amounts, preferably less than 5 mol% and in particular less than 1 mol%, of one or more other alkenes copolymerised therewith,

such as propylene, butene, pentene, hexene, 4-methylpentene, octene and the like. The polyethylene can also contain minor amounts, preferably at most 25% by weight, of one or more other polymers, in particular a 1-alkene polymer, such as polypropylene, polybutene or a copolymer of propylene with a minor amount of ethylene.

According to the invention a stretchable ethylene polymer is understood to be an ethylene polymer having a maximum draw ratio of at least 20. According to the invention, the maximum draw ratio is determined as follows. A layer of ethylene polymer powder 2 mm high is compressed in a circular mould having a diameter of 5 cm for 5 minutes at room temperature under a weight of 50,000 kg. The circular film obtained is then post-pressed at 130°C for 10 minutes under a weight of 100,000 kg in a flat press. A halter-shaped specimen having a length of 10 mm between the shoulders is punched from the film obtained in this way. This specimen is stretched in a Zwick 1445 Tensile Tester at a temperature of 130°C at a rate of 10 mm/min until the specimen breaks. The maximum draw ratio is determined as the quotient of the length of the section of the specimen between the shoulders when breakage occurs in the specimen and the length thereof prior to stretching (10 mm). Preferably, the maximum draw ratio is at least 30 and more particularly at least 40.

The ethylene polymer according to the invention can contain non-polymer materials, such as solvents and fillers. The amount of these materials can be up to 60% by volume with respect to the ethylene polymers.

In order to improve the mechanical properties of the articles and/or to reduce the diameter of said articles, the articles according to the invention can be stretched in the conventional way. This can be effected in the solid phase, below the melting point of the thermoplastic polymer material, or in the melt phase. With regard to the stretching of UHMWPE see, for example, "Ultra high modulus Polymers", Ed. A. Ciferri and I.M. Ward, Applied Science

Publishers, London (1977), p. 1-116, 321-356.

The ethylene polymer according to the invention is particularly suitable for the preparation of an article having a tensile strength of at least 1.2 GPa and a modulus of elasticity of at least 80 GPa from high molecular weight ethylene polymer, pulverulent ethylene polymer being subjected, at a temperature below the melting point of the ethylene polymer, to a pressure treatment at a pressure of at least 10 MPa, an article composed of ethylene polymer being formed, which is then stretched at a temperature of at least 100°C.

The invention will be illustrated below with the aid of illustrative embodiments. The measurement data reported in the experimental section with respect to the tensile strength ( $\sigma$ ) and modulus of elasticity (E) were determined in accordance with ISO-527 type 2 using a clamped length of 2 cm and a stretching rate of  $1.7 \cdot 10^{-2} \text{ s}^{-1}$ .

20

### Experiments

#### Example I

##### A. Polymerisation

The catalyst used for the polymerisation of ethylene was a highly active Ziegler/Natta catalyst of type UM-1<sup>R</sup> from Toho Titanium. This is a titanium-containing catalyst on a support of magnesium chloride. The specific surface area of the catalyst was 6 m<sup>2</sup>/g. The catalyst was used in the form of a slurry in anhydrous heptane. The concentration of the catalyst in the slurry is 0.050 g/ml.

30 Litres of dry heptane were metered, under dry nitrogen, into a polymerisation reactor which had a volume of 55 litres and was provided with a stirrer. The reactor was then heated to 60°C, with stirring (330 rpm). 30 ml of a 2 mmol/l solution of triethylaluminium in heptane was then metered in and subsequently 80.3 ml of catalyst slurry (4.047 g) was supplied. Ethylene was then introduced into the reactor until a total pressure of 0.17 MPa was obtained.



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The ethylene pressure was 0.07 MPa. During the polymerisation, the pressure was kept constant by supplying ethylene. After a reaction time of 127 minutes, the pressure in the reactor was let down. The slurry from the reactor was then filtered. The filtration residue was rinsed with heptane while passing through nitrogen. The powder was then dried at room temperature, successively for 12 hours under nitrogen and for 12 hours under vacuum. The yield was 3,745 g of polyethylene. The productivity was 925 g of polyethylene per g of catalyst. The bulk density was 195 kg/m<sup>3</sup>. The intrinsic viscosity (IV) is 19 dl/g.

15 B. Analysis of the polymer powder

1. Maximum draw ratio of the polymer powder

A layer of ethylene polymer powder 2 mm high was compressed in a circular mould having a diameter of 5 cm for 5 minutes at room temperature under a weight of 50,000 kg. The circular film obtained was then post-pressed at 130°C for 10 minutes under a weight of 100,000 kg in a flat press. A halter-shaped specimen having a length between the shoulders of 10 mm was punched from the film thus obtained. This specimen was stretched in a Zwick 1445 Tensile Tester at a temperature of 130°C, at a rate of 10 mm/min, until the specimen broke. The maximum draw ratio was determined as the quotient of the length of the section of the specimen between the shoulders when breakage occurs in the specimen and the length thereof prior to stretching (10 mm). The tensile strength ( $\sigma$ ) and the modulus of elasticity (E) were determined on the stretched specimens. The maximum draw ratio was 43. The results are shown in Table 1.

2. Lamella thickening factor

35 For determination of the lamella thickening factor the polymer powders were embedded in a resin mixture of butylmethacrylate and methylmethacrylate (70:30). After fixation with RuO<sub>4</sub> in a known manner, slices having a thickness of 70 nm were cut at room temperature.

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Transmission electronmicroscopic (TEM) photographs were taken of the powders before and after a thermal treatment of 75 hours at 125°C. The thicknesses of the lamellae were measured on the TEM-photographs. The lamella thickness was defined as the average thickness of 10 lamellae. The lamella thickness before thermal treatment was designated as  $L_b$ , the lamella thickness after thermal treatment as  $L_a$ . The lamella thickening factor  $Q$  was calculated using the relation:  $Q = (L_a - L_b) / L_b$ .

#### C. Processing of the ethylene polymer

Stretched films were prepared with the aid of a co-extrusion technique as described in L. H. Wang, S. Ottani, R.S. Porter in Polymer 1991, Volume 3, No. 10, pages 1776-81. The draw ratio ( $\lambda$ ), the tensile strength ( $\sigma$ ) and the modulus of elasticity ( $E$ ) are shown in Table 2.

#### Example II

##### A. Polymerisation

The polymerisation was carried out as in example I. The catalyst used was a Ziegler/Natta catalyst of the Lynx 705<sup>R</sup> type from Catalyst Resources Inc. Before use as catalyst, the catalyst was ground in a Dyno-mill<sup>R</sup> until a particle size  $D_{50}$  of 6.1  $\mu\text{m}$  was obtained. The specific surface area of the ground catalyst was 27  $\text{m}^2/\text{g}$ . The particle size was determined with the aid of a Malvern<sup>R</sup> particle analyser. The amount of catalyst slurry metered in for the polymerisation was 0.45 g and the reaction time was 398 minutes. The yield was 4,163 g of polyethylene. The productivity was 9,251 g of polyethylene per g of catalyst. The bulk density was 254  $\text{kg}/\text{m}^3$ .

##### B. Analysis of the polymer powder

The determination was carried out as in Example I and resulted in a maximum draw ratio of 32.

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C. Processing of the polymer powder

This was carried out in accordance with Example I.

5 The results are given in Table 2.

Comparative experiment A

Polymer powder of the Hostalen GUR 212<sup>R</sup> type from Hoechst was used for the analysis according to Example I,  
 10 section B, and processing according to Example I, section C. The results are given in Tables 1 and 2.

Comparative experiment B

A polymer powder was prepared and processed under  
 15 the conditions indicated in Example I, but the catalyst used was a highly active titanium catalyst having a specific surface area of 223 m<sup>2</sup>/g and a Mg/Ti molar ratio of 12.7. The results are given in Tables 1 and 2.

20 Table 1: Results of examples and comparative experiments. Intrinsic viscosity (IV), bulk density (BD), specific surface area (SA), amount of catalyst residues, lamella thickening factor (Q), maximum draw ratio ( $\lambda_{max}$ ), tensile strength ( $\sigma$ ) and  
 25 modulus of elasticity (E).

Exp. No.	SA (m <sup>2</sup> /g)	IV (dl/g)	BD (kg/m <sup>3</sup> )	Cat. res. (ppm)	Q (-)	$\lambda_{max}$ (-)	$\sigma$ (GPa)	E (GPa)
30								
I	6	19	195	30	2.1	43	0.85	64
II	27	16	254	2	2.1	32	0.73	41
A	-*	16	200	10	1.5	4	0.04	1
35 B	223	16	307	11	1.5	18	0.4	30

\* catalyst not available

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Table 2: Results of solid state co-extrusion

5	Exp. No.	$\lambda$	$\sigma$	E
		(-)	(GPa)	(GPa)
		<hr/>		
10	I	89	1.9	140
	II	96	1.4	115
	A	8	0.1	2
	B	40	0.6	75

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C L A I M S

- 5 1. Ethylene polymer having an intrinsic viscosity of at least 4 dl/g, characterised in that the ethylene polymer has a maximum draw ratio of at least 20, is pulverulent, has a bulk density of at most 300 kg/m<sup>3</sup> and has an amount of catalyst residues of less than 50 ppm.
- 10 2. Ethylene polymer having an intrinsic viscosity of at least 4 dl/g, characterized in that the ethylene polymer is pulverulent, has a bulk density of at most 300 kg/m<sup>3</sup> and has an amount of catalyst residues of less than 50 ppm and a lamella thickening factor of at least 1.5, measured after a thermal treatment of 75 hours at 125°C.
- 15 3. Ethylene according to claim 2, characterized in that it has a lamella thickening factor of at least 2.0.
4. Ethylene polymer according to any one of Claims 1-3, characterised in that it has a bulk density of at most 20 250 kg/m<sup>3</sup>.
5. Ethylene polymer according to any one of Claims 1-4, characterised in that it has an amount of catalyst residues of less than 25 ppm.
- 25 6. Method for the preparation of a pulverulent ethylene polymer having an intrinsic viscosity of at least 4 dl/g through polymerisation of ethylene or of a mixture of ethylene and not more than 5 mol% higher olefins at a temperature below 80°C and an ethylene pressure of at most 0.2 MPa in the presence of a catalyst, characterised in that the catalyst is a transition 30 metal-containing catalyst having a specific surface area of at most 150 m<sup>2</sup>/g.
7. Method according to Claim 6, characterised in that the catalyst is a titanium-containing catalyst having a specific surface area of at most 50 m<sup>2</sup>/g. 35
8. Method according to Claim 7, characterised in that the catalyst is a titanium-containing catalyst having a specific surface area of at most 10 m<sup>2</sup>/g.

10. Method according to any one of Claims 6-8, characterised in that the ethylene pressure is at most 0.15 MPa.
- 5 11. Method according to Claim 10, characterised in that the ethylene pressure is at most 0.1 MPa.
12. Method according to any one of Claims 6-11, characterised in that the catalyst has an activity of at least 800 g of polyethylene per gram of catalyst under
- 10 polymerisation conditions such that the ethylene pressure is 0.07 MPa and the polymerisation temperature 60°C.
13. Method according to Claim 12, characterised in that the catalyst is a titanium-containing catalyst applied to a
- 15 support which comprises magnesium chloride.
14. Method according to Claim 13, characterised in that the Mg/Ti molar ratio in the catalyst is at least 5.
15. Method according to Claim 14, characterised in that the Mg/Ti molar ratio in the catalyst is at least 10.
- 20 16. Method for the preparation of an article having a tensile strength of at least 1.2 GPa and a modulus of elasticity of at least 80 GPa from high molecular weight ethylene polymer, pulverulent ethylene polymer being
- 25 subjected, at a temperature below the melting point of the ethylene polymer, to a pressure treatment at a pressure of at least 10 MPa, an article composed of ethylene polymer being formed which is then stretched at a
- temperature of at least 100°C, characterised in that an ethylene polymer according to any one of Claims 1-5 is
- 30 used.
14. Method, ethylene polymer or article composed of ethylene polymer as essentially described and/or obtained with the aid of examples.

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) <sup>6</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl.5	C 08 F 10/02	C 08 F 4/02 C 08 F 4/62
II. FIELDS SEARCHED		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
Int.Cl.5	C 08 F	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>		
III. DOCUMENTS CONSIDERED TO BE RELEVANT <sup>9</sup>		
Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
X	EP,A,0358264 (ENICHEM) 14 March 1990, see claims; examples 18-24 ---	6,10,15
X	NL,A,7809251 (MITSUI) 13 March 1979, see claims 1-6; examples ---	6,7,10,12,15
A	WO,A,8703288 (DU PONT) 4 June 1987, see claims; comparative example F (cited in the application) ---	
A	EP,A,0212519 (BASF) 4 March 1987, see example 1 --- -/-	
<p><sup>10</sup> Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&amp;" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
13-05-1993	18.06.93	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	R. DE ROECK	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category <sup>a</sup>	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	<p>Polymer Science USSR, vol. 16, no. 12, 1974, A.A. BAULIN et al.: "The effect of the carrier type and structure used for the <math>\text{TiCl}_4\text{-Al}(\text{C}_2\text{H}_5)_3</math> carrier catalyst of ethylene polymerization", pages 2688-2694</p> <p>-----</p>	



**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.**

NL 9300026  
SA 69918

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 08/06/93. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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WO-A- 8703288	04-06-87	US-A- 4769433 CA-A- 1297232 EP-A- 0248056 JP-T- 62502477 US-A- 5036148	06-09-88 10-03-92 09-12-87 24-09-87 30-07-91
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